CORRELATION OF STRUCTURE AND REACTIVITY
IN ALKYLARENE THERMOLYSIS

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INTRODUCTION
There is an industrial trend toward developing molecular-level process models for the conversion of hydrocarbon-containing feedstocks. The development of such models has been motivated by a desire for more efficient processes and improved product quality, and to an extent by environmental regulations. Recent and continuing advances in analytical chemistry, which provide increasingly detailed structural descriptions of complex materials, and advances in computing have fueled the formulation of these increasingly complex models. An integral part of such models is a set of correlations that relates the reactivity (e.g., kinetics and product distributions) of a given portion of the feedstock to its chemical structure.

Polycyclic n-alkylaromatic moieties are important structural features of feedstocks such as crude oils, bituminous sands, kerogens, asphaltenes, and coals,[1-5] and recently the thermal chemistry of representative model compounds has been explored.[6-11] An interesting observation that arose from these pyrolysis experiments was that the very strong aryl-alkyl C-C bond was susceptible to hydrogenolytic cleavage. We developed a quantitative correlation that related the rate of this aryl-alkyl bond cleavage in long-chain n-alkylarenes to the respective localization energies through Dewar reactivity numbers calculated from perturbational molecular orbital (PMO) theory.[8] In this paper we extend the previous analysis to develop a similar structure-reactivity correlation for methylarenes based on the set of methylaromatics displayed in Figure 1.

EXPERIMENTAL
1-Methylnaphthalene (1-MN), 1-methylanthracene (1-MA), 2-methylanthracene (2-MA), and 9-methylanthracene (9-MA) were pyrolyzed at temperatures between 350°C and 450°C. All chemicals were obtained from Aldrich. The pyrolyses were conducted in constant-volume, 316 stainless steel, micro-batch reactors. The reactors were constructed from one Swagelok port connector and two Swagelok end caps, and they had a nominal volume 0.6 ml. Previous work established that the reactor material did not alter the experimental results.[10] As an additional test for catalytic activity by the reactor walls, we conducted several pyrolyses in the presence of stainless steel filings and saw no appreciable effect on conversion and product selectivities.

The batch reactors were typically loaded with 10 mg of the model compound and 10 mg of an internal standard and sealed in a nitrogen-filled glovebox. After being loaded and closed, the reactors were placed in an isothermal, fluidized sandbath. Upon reaching the desired holding time, the reactors were removed from the fluidized bath, and the reaction was quenched. The products were recovered by repeated extraction with benzene.

The reaction products were analyzed by gas chromatography (GC) and gas chromatography-mass spectrometry. The GC analysis used a Hewlett Packard 5890 instrument equipped with a flame ionization detector (FID). The reaction products were identified by comparing their GC retention times with those of authentic standards and by inspection of their mass spectra. Product molar yields, calculated as the number of moles of product formed divided by the number of moles of the reactant initially loaded in the reactor, were obtained from the GC analyses using experimentally determined FID response factors. We estimate the uncertainty in these yields to be about 20%. Further analytical details have been given previously.[6-10]

RESULTS

In the following section, we present the results from the pyrolysis of 1-MA, 2-MA, and 9-MA. Tables I-III give representative data for these compounds in terms of the yields of the major products and selected minor products.

1-Methylanthracene (1-MA): The neat pyrolysis of 1-MA was conducted at 400°C, 425°C, and 450°C for batch holding times up to 300 minutes. Table 1 provides representative experimental data obtained under different reaction conditions. The products from 1-MA pyrolysis were anthracene, 9,10-dihydroanthracene (DHA), 1,2,3,4 tetrahydroanthracene (THA), 1-methyl-9,10-dihydroanthrancene (1-MDHA), 9-methylanthracene, 5 dimethylanthracene (DMA) isomers, and benzene-insoluble char. We were not able to determine the specific locations of the methyl groups in the dimethylanthracene isomers so we have simply identified these isomers as I, II, III, IV, and V.

Anthracene was the most abundant product at all reaction conditions, and its molar yield generally increased with batch holding time at all three temperatures. The highest anthracene yield was 31%, which was obtained at a batch holding time of 120 minutes for the pyrolysis at 450°C. At conversions less than 50%, 1-MDHA was the second most abundant product, but at higher conversions its yield was low. For example, at 425°C the molar yield for 1-MDHA reached a maximum value of 2.9% at a holding time of 60 minutes, and it subsequently decreased to 1.4% at 300 minutes. This same behavior (i.e., the presence of a maximum) was also observed for each of the dimethylanthracene isomers and 9-methylanthracene. Such behavior was not observed for the yields of the remaining minor products, DHA and THA. Rather, the molar yields of these products were very low at short batch holding times, but they increased steadily with time to become significant minor products. For example, at 425°C the molar yields of DHA and THA were 0.5% and 0.1%, respectively at 60 minutes, but these yields increased to 3.5% and 2.2%, respectively, at 300 minutes.

2-Methylanthracene (2-MA): Table II lists the products' molar yields obtained from the pyrolysis of 2-MA at 400, 425, and 450°C. The major products were anthracene and 2-methyl-9,10-dihydroanthracene (2-MDHA). The minor products included three dimethylanthracene isomers. A benzene-insoluble char was also observed. The highest conversion of 2-MA, 87%, occurred at the most severe reaction conditions employed (200 minutes at 450°C).

The molar yield of anthracene steadily increased with batch holding time. The highest molar yield (20%) for this compound was obtained at 450°C for a batch holding time of 200 minutes. The behavior of the 2-MDHA yield was analogous to that of the 1-MDHA yield in 1-MA pyrolysis. For example, at 450°C the molar yield of 2-MDHA increased to 5.8% at 75 minutes and subsequently decreased thereafter.

9-Methylanthracene (9-MA): The neat pyrolysis of 9-MA was conducted at 350, 375, and 400°C for batch holding times up to 180 minutes. Table III provides representative data from these experiments. The major product from 9-MA pyrolysis was always anthracene. The highest yield of anthracene, 42%, was obtained at the most severe conditions (90 minutes at 400°C), and the corresponding conversion of 9-MA was 85%. DHA and two dimethylanthracene isomers were observed as minor products. The molar yield of DHA increased with batch holding time until it reached a maximum, and then it subsequently decreased. At 400°C, for example, the maximum molar yield for this compound was 5.1% at 30 minutes.

PYROLYSIS PATHWAYS

We used the Delplot technique to deduce a general reaction network for the pyrolysis of the methylanthracenes studied.[12] This methodology determines the order of appearance of products in a reaction network through the examination of their initial selectivities, where the selectivity is calculated as the molar yield divided by the reactant conversion. These initial selectivities are determined as the y-intercept of the selectivity versus conversion curve for each product. Typically, products that have a non-zero initial selectivity are primary products (those that arise directly from the reactant), and they are the first to appear in the reaction network. Products that have zero initial selectivities are generally secondary and higher order products.

Figure 2 displays the Delplots for 1-MA pyrolysis. The discrete points are the experimental data, and the curves are drawn to convey the trends in these data. Figure 2a presents the selectivities to anthracene, DHA, and 1-MDHA as a function of conversion. Analysis of the y-intercepts for each of the products reveals that anthracene and 1-MDHA have initial selectivities of 0.19 and 0.14, respectively, and that the initial selectivity for DHA is essentially zero. This signifies that anthracene and 1-MDHA are primary products, and DHA is a secondary or higher order product. Figure 2a also shows that the selectivity to 1-MDHA decreases with conversion, which implies that 1-MDHA undergoes secondary decomposition at higher conversions. In this light, it is interesting to observe that the DHA selectivity increases with conversion, and that one possible route to its formation is dealkylation of 1-MDHA.

The Delplots for the five dimethylanthracene isomers are displayed in Figure 2b. The initial selectivity for each of these compounds is non-zero, which indicates that each is a primary product. The selectivity to each of these compounds decreases with the 1-MA conversion, which may indicate that secondary decomposition occurs.

We conducted similar reaction pathway analyses using the pyrolysis product data for the other two methylanthracenes to develop a general reaction network for the pyrolysis of methylanthracenes. This pyrolysis network is shown in Figure 3. The network includes the primary conversion of each of the methylanthracenes to anthracene and to dimethylanthracene isomers. This portion of the pathway involves reversible steps. 1-MA and 2-MA can also undergo primary reaction to 1-MDHA and 2-MDHA, respectively, and DHA can form through the secondary reactions of 1-MDHA, 2-MDHA, and anthracene.

STRUCTURE AND REACTIVITY

Our development of a structure-reactivity correlation for the compounds in Figure 1 will focus on the pathway through which the aryl-alkyl C-C bonds are cleaved. The mechanism responsible for this cleavage involves a hydrogenolysis reaction in which the methyl substituent is displaced by hydrogen,[6,7] but the mechanistic details remain unresolved. Possible mechanisms include hydrogen atom ipso-substitution,[13] molecular disproportionation,[14,15] and radical hydrogen transfer.[16,17] Each of these mechanisms involves the transfer of a hydrogen atom from a donor to the *ipso* position of the methylanthracene thereby engendering aryl-alkyl bond cleavage. Thus, in essence, this reaction involves a substitution reaction in which the methyl group is replaced by a hydrogen atom.

For aromatic substitution reactions involving a family of arenes, the differences in the activation energies are likely due to the changes in the differences between the energies of the delocalized electrons in the reactants and in the transition state (i.e., $\Delta E^{\ddagger}_{\pi}$, the delocalization energy of activation). From PMO theory and the Evans-Polanyi principle, we expect the differences in activation energies to be proportional to the differences in the energies of reaction, which in turn can be attributed to the change in energy of the delocalized electrons (π-energy of the system, ΔE_{π}) provided there is little or no change in energy of the localized bonds and in solvation.[18-20] The result of this analysis allows us to write Equation 1, where α is the Evans-Polanyi factor.

$$\Delta E^{\ddagger}_{\pi} \cong \Delta E_a = constant + \alpha \, \Delta E_{\pi} \qquad (1)$$

For even alternant hydrocarbons, ΔE_{π} can be calculated readily from PMO theory as

$$\Delta E_{\pi} = 2 \, \beta \, (a_{or} + a_{os}) = \beta N_t \qquad (2)$$

where β is the resonance integral, and a_{or} and a_{os} are the coefficients of the non-bonding molecular orbitals at the positions adjacent to the position of substitution, which is denoted by the subscript t.[18,19] The value of β should be the same for a given reaction family since the structures of the transition states should be similar. The quantity $2(a_{or} + a_{os})$ is defined as the Dewar reactivity number, N_t, and the values for the compounds used in the present study were given in Figure 1 . These Dewar numbers are for the aromatic position bearing the methyl substituent.

Combining Equations 1 and 2 shows that

$$\Delta E_a = constant + \alpha \beta N_t \qquad (3)$$

Equation 3 suggests that a semilog plot of the reaction rate constants for aromatic substitution reactions as a function of the Dewar reactivity number, N_t, should be linear. We desired to employ the Dewar reactivity number as a correlating parameter, but we could not calculate the value of the rate constant because the precise form of the hydrogenolysis rate law is unknown. Thus, we chose to employ initial rates in the correlation. These rates were calculated as the initial slope of the arene molar yield vs. time curve. Figure 4 displays the natural logarithm of this initial rate of aryl-alkyl bond cleavage at 400°C as a function of the Dewar reactivity number for the methylarenes used in this study and for 1-methylpyrene (1-MP).[9]

Two linear correlations exist for the data presented in Figure 4. The first is for the methylarenes in which the position bearing the methyl group and the position with the lowest Dewar number (i.e., most reactive position) coincide, and the second is for the three methylanthracenes, compounds in which these positions do not necessarily coincide. These two distinct lines emerge because there are two key features that principally control the rate of hydrogenolysis. The first is the rate at which hydrogen is added to and CH_3 removed from the substituted position in the methylarene. This rate should correlate with the Dewar number of the position bearing the substituent. The second feature is the rate at which hydrogen is added to any position on the methylarene to form potential radical hydrogen donors, which can subsequently engender hydrogenolysis. This rate, to a first approximation, should correlate with the Dewar number of the most reactive position in the methylarene. Thus, the two key Dewar numbers for a polycyclic alkylarene are the one for the substituted position and the one for the most reactive position (i.e., the lowest one). For compounds where these numbers coincide, a single line is expected. Thus, the data for 9-MA, 1-methylpyrene (1-MP), and 1-methylnaphthalene (1-MN) fall on a single line. For an alkylarene in which these Dewar numbers differ (i.e., 1-MA, 2-MA) a different correlation is expected. This expectation is realized by the methylanthracene data in Figure 4.

Each peripheral carbon atom in a polynuclear aromatic can accept hydrogen from a donor, and each carbon atom has its own susceptibility for hydrogen addition, which is dependent upon its intrinsic reactivity. The Dewar reactivity number provides a numerical measure of the ease of hydrogen addition to a given position. Positions with lower Dewar numbers accept hydrogen more readily than do positions with higher Dewar numbers. Thus, the rates of hydrogenolysis for methylarenes having the methyl group at the position possessing the highest reactivity (e.g., lowest Dewar number) should correlate with the Dewar number of that position because a majority of the hydrogen addition will be to the ipso-position. This correlation appears as line 1 in Figure 4.

For methylarenes in which the methyl group is not substituted on the position of highest reactivity, hydrogen adds more rapidly to non-ipso positions to form hydroaromatic radicals than it adds to the ipso position. These hydroaromatic radicals can engender subsequent hydrogenolysis through radical hydrogen transfer steps. Thus, methylarenes with highly reactive non-ipso positions can undergo hydrogenolysis at a rate that is higher than expected from the Dewar number of the ipso position. The presence of these more reactive non-ipso positions provides additional modes for engendering hydrogenolysis. This behavior is exhibited in the methylanthracenes because the 9-position is highly reactive, and it can readily accept hydrogen to form a 9-hydroanthracyl radical. These hydroaromatic radicals can then transfer hydrogen to the ipso position, via RHT for instance, and engender hydrogenolysis. This increase in the H-donor pool concentration increases the rate of demethylation above what it would be if the highly reactive 9 position were absent. Thus, the rates of aryl-alkyl C-C bond cleavage for 1-MA and 2-MA fall above line 1 in Figure 4.

The insight gained from Figure 4 can be used for predictive purposes. Consider two methylarenes that have identical Dewar numbers for the position bearing the methyl substituent. In the first compound the position of highest reactivity and the position bearing the substituent coincide, whereas in the second compound they do not. The rate of demethylation

will be greater in the second compound because additional modes of hydrogen transfer involving hydroaromatic radicals are available.

SUMMARY AND CONCLUSIONS

1. The pyrolysis of methylanthracenes leads to anthracene as the major product. Minor products include methyl-9,10-dihydroanthracenes, 9,10-dihydroanthracene, and dimethylanthracenes.

2. Anthracene, dimethylanthracenes, and methyl-9,10-dihydroanthracenes were primary products of methylanthracene pyrolysis. Dihydroanthracene and methylanthracene isomers were secondary products.

3. The rates of aryl-alkyl bond cleavage for methylanthracene pyrolyses were correlated with the Dewar reactivity numbers for the peripheral aromatic carbon bearing the methyl group. A second correlation was deduced for the rate of demethylation of 9-methylanthracene, 1-methylpyrene, and 1-methylnaphthalene. The existence of two distinct structure-reactivity correlations is consistent with the governing hydrogen transfer mechanisms.

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Table I: Product Molar Yields from 1-Methylanthracene

Temp (°C)	400	400	400	400	400	425	425	425	425	425	450	450	450	450	450
Time (min)	60	150	200	240	300	30	60	120	150	300	30	90	120	150	300
Anthracene	2.9%	9.3%	4.8%	10.3%	16.7%	4.0%	10.8%	16.4%	23.8%	26.8%	14.7%	26.3%	30.9%	28.8%	23.3%
DHA	0.0%	0.6%	0.2%	0.7%	1.5%	0.0%	0.5%	1.2%	2.7%	3.5%	0.9%	2.6%	3.4%	3.2%	3.4%
THA	0.0%	0.2%	0.0%	0.3%	0.8%	0.0%	0.1%	0.5%	1.4%	2.2%	0.2%	1.1%	1.7%	1.6%	1.7%
DMA I	0.3%	0.9%	0.5%	1.0%	1.2%	0.4%	1.0%	1.2%	1.0%	0.5%	1.1%	1.0%	0.6%	0.3%	0.0%
DMA II	0.3%	1.1%	0.5%	1.2%	1.8%	0.4%	1.2%	1.7%	2.1%	1.3%	1.5%	2.1%	1.4%	0.9%	0.0%
DMA III	0.7%	2.0%	1.1%	2.2%	2.6%	0.9%	2.3%	2.5%	2.1%	0.7%	2.5%	2.0%	0.0%	0.0%	0.0%
DMA IV	0.1%	0.3%	0.1%	0.2%	0.3%	0.1%	0.2%	0.3%	0.3%	0.0%	0.4%	0.4%	0.3%	0.0%	0.0%
DMA V	1.0%	1.3%	1.4%	1.0%	0.7%	1.3%	1.5%	0.7%	0.4%	0.0%	0.9%	0.3%	0.0%	0.0%	0.0%
1-MDHA	2.3%	3.4%	2.7%	2.9%	3.3%	2.0%	2.9%	2.3%	2.2%	1.4%	2.3%	1.9%	1.4%	1.1%	0.1%
9-MA	0.0%	0.5%	0.1%	0.5%	0.9%	0.0%	0.6%	0.8%	0.9%	0.3%	0.6%	0.8%	0.3%	0.3%	0.0%
1-MA	74.9%	56.3%	75.6%	47.4%	36.6%	81.4%	66.1%	32.7%	22.1%	9.5%	43.3%	20.7%	9.5%	8.2%	2.7%

Table II: Product Molar Yields from 2-Methylanthracene

Temp (°C)	400	400	400	400	400	425	425	425	425	425	450	450	450	450	450
Time (min)	15	60	90	120	130	30	45	60	150	200	60	75	90	160	200
Anthracene	0.1%	0.2%	0.7%	1.0%	1.2%	2.5%	3.8%	4.3%	6.7%	8.9%	6.5%	9.5%	11.3%	14.6%	19.7%
DMA I	0.1%	0.4%	0.7%	0.9%	0.8%	0.7%	1.7%	2.1%	0.8%	1.2%	0.7%	1.1%	1.3%	0.0%	1.6%
DMA II	0.1%	0.1%	0.1%	0.1%	0.0%	0.1%	0.2%	0.0%	2.9%	3.3%	2.5%	3.1%	3.7%	0.0%	0.0%
DMA III	0.2%	0.4%	0.4%	0.5%	0.4%	0.4%	1.1%	1.4%	1.7%	1.4%	1.6%	0.0%	1.6%	0.0%	0.0%
2-MDHA	1.7%	2.5%	3.4%	3.8%	3.5%	1.3%	3.4%	4.7%	5.9%	4.7%	4.9%	5.8%	5.3%	4.6%	0.0%
2-MA	100.6%	95.0%	87.6%	82.3%	66.7%	81.8%	78.8%	70.2%	67.0%	53.5%	67.2%	61.2%	44.7%	37.0%	13.3%

Table III: Product Molar Yields from 9-Methylanthracene

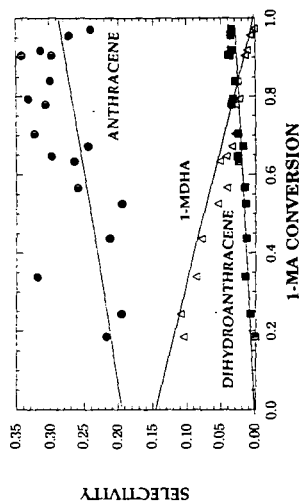| Temp (°C)	350	350	350	350	350	375	375	375	375	375	400	400	400	400	400
Time (min)	15	30	60	100	180	15	30	45	60	90	15	30	45	60	90
Anthracene	7.2%	1.9%	2.9%	3.4%	4.6%	6.4%	11.6%	15.3%	20.9%	20.6%	9.0%	17.9%	34.5%	33.1%	42.0%
DHA	1.0%	0.0%	0.2%	0.6%	0.2%	0.5%	0.8%	1.1%	1.2%	1.1%	2.6%	5.1%	2.2%	2.3%	1.1%
DMA I	0.7%	0.0%	0.0%	0.4%	0.5%	0.8%	1.4%	2.0%	2.3%	1.9%	1.6%	2.5%	2.4%	1.4%	1.0%
DMA II	2.5%	0.7%	1.1%	1.1%	1.7%	0.7%	2.6%	2.5%	2.4%	0.8%	1.0%	1.4%	2.5%	1.9%	1.9%
9-MA	94.3%	122.0%	115.7%	106.0%	129.0%	84.0%	78.3%	78.3%	61.8%	39.9%	53.4%	34.8%	30.8%	18.1%	15.3%

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Figure 2a: 1-MA Selectivity to Anthracene, 9,10-Dihydroanthracene (DHA), and 1-Methyl-9,10-dihydroanthracene (1-MDHA).
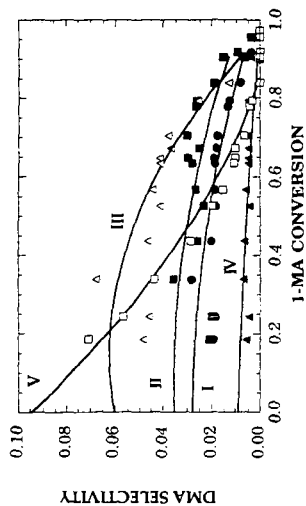

**Figure 2b:** 1-MA Selectivity to Dimethylanthracene (DMA) Isomers (I-V).

Model Compounds	Name	Dewar Number
	1-Methylnaphthalene (1-MN)	1.81
	1-Methylanthracene (1-MA)	1.57
	2-Methylanthracene (2-MA)	1.89
	9-Methylanthracene (9-MA)	1.26
	1-Methylpyrene (1-MP)	1.51

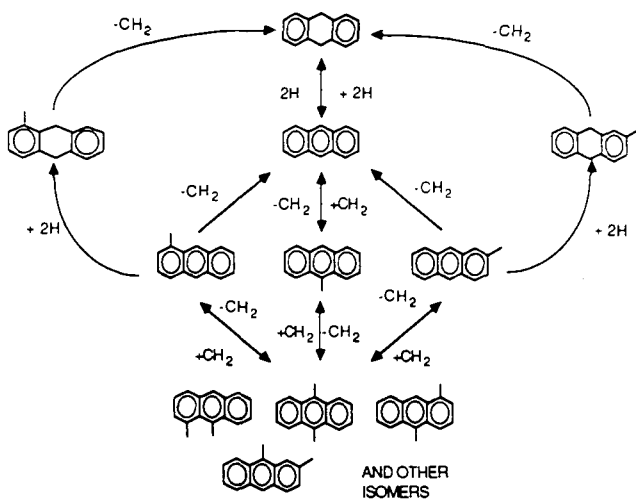*Figure 1:* Heavy Feedstock Model Compounds.

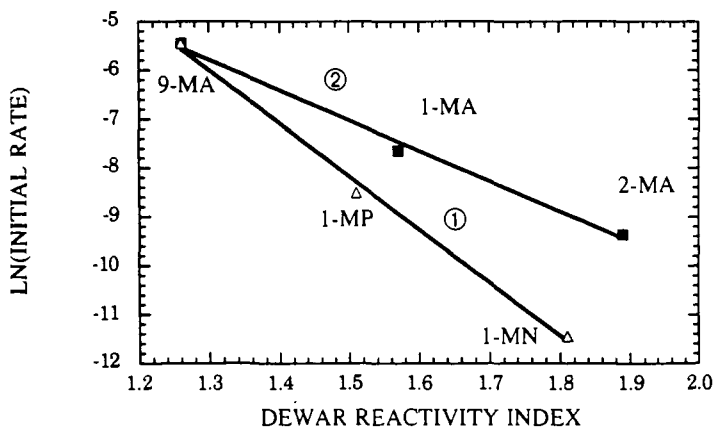**Figure 3:** Pyrolysis Network for Methylanthracenes.

Figure 4: Correlation of Initial Rate of Demethylation in Methylarene Pyrolysis with Dewar Reactivity Numbers